FRACTIONAL CRYSTALLIZATION LABORATORY TESTING FOR INCLUSION AND CO-PRECIPITATION WITH ACTUAL TANK WASTE

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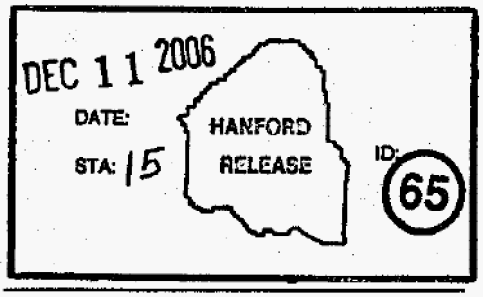
Abstract: Laboratory-scale tests of the fractional crystallization process for contaminant inclusions and co-precipitation were conducted with actual tank waste samples in a hot cell at the 222-S Laboratory. The primary factors that influence the separation efficiency are solid/liquid separation efficiency, contaminant inclusions, and co-precipitation. This is a report of test results for the latter two factors in NaNO3, Na2CO3, Na6CO3(SO4)2, and Na2C2O solid phases.



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1. INTRODUCTION

Fractional crystallization is being considered as a pretreatment method to support supplemental treatment of retrieved single-shell tank (SST) saltcake waste at the Hanford Site. The goal of the fractional crystallization process is to optimize the separation of the radioactivity (radionuclides) from the saltcake waste and send it to the Waste Treatment and Immobilization Plant and send the bulk of the saltcake to the supplemental treatment plant (bulk vitrification). The primary factors that influence the separation efficiency are (1) solid/liquid separation efficiency, (2) contaminant inclusions, and (3) co-precipitation. This is a report of testing for factors (2) and (3) with actual tank waste samples. For the purposes of this report, contaminant inclusions are defined as the inclusion of supernatant, containing contaminating radionuclides, in a pocket within the precipitating saltcake crystals. Co-precipitation is defined as the simultaneous precipitation of a saltcake crystal with a contaminating radionuclide. These two factors were tested for various potential fractional crystallization product salts by spiking the composite tank waste samples (SST Early or SST Late, external letter CH2M-0600248, "Preparation of Composite Tank Waste Samples for EM-21 Project") with the desired target salt and then evaporating to precipitate that salt. SST Early represents the typical composition of dissolved saltcake early in the retrieval process, and SST Late represents the typical composition during the later stages of retrieval. See Table 2-1 for a summary of the compositions of both feed solutions.

Descriptions and historical background, theory, and application of the fractional crystallization process have been described in prior reports (RPP-RPT-26474, *Fractional Crystallization of Waste from Tank 241-S-112;* RPP-RPT-27239, *Hanford Medium/Low Curie Waste Pretreatment Project – Phase I Laboratory Report; and* RPP-RPT-31352, *Fractional Crystallization Flowsheet Tests with Actual Tank Waste).* Briefly, the liquid waste formed during retrieval of saltcake waste from single-shell tanks represents the feed for the fractional crystallization process. Within the fractional crystallization plant, the waste is evaporated to form sodium salt crystals. The bulk of the radionuclides—especially ^{137}Cs, ^{99}Tc, and ^{129}I—remain in the liquid phase. The slurry is filtered or centrifuged and the solids are washed to remove interstitial liquid. The high-activity filtrate or centrate is routed to a double-shell tank for storage and the spent wash solution is recycled to the evaporator. The washed solids are dissolved to create feed for a supplemental treatment and disposal facility.

1.1 TEST SUMMARY AND RESULTS

Four sodium salts were chosen for inclusion and co-precipitation testing:

a. Sodium nitrate ($NaNO_3$) in SST Early composite.
b. Sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$) in SST Early composite.
c. Burkeite [$Na_6CO_3(SO_4)_2$] in SST Early composite.
d. Sodium oxalate ($Na_2C_2O_4$) in SST Late composite.

Salt items a, b, and c were chosen since they are the three major product salts identified in Phase I testing with SST Early simulants. Salt item d was chosen as being a major phase on the evaporation of SST Late composite (see Table 2-1).

Test results showed that the radionuclides ^{137}Cs, ^{99}Tc, and ^{129}I remain in the liquid phase with very little inclusion and that much of the ^{90}Sr co-precipitated with the solid phase and could not be washed out.

1.2 PRIOR TESTS WITH ACTUAL TANK WASTE

Prior studies (WHC-EP-0915, *Clean Salt Process Final Report*) reported that contaminant inclusion of ^{137}Cs in $NaNO_3$ was 0.14% of the total present in the feed and was carried out in acid conditions. The study reported here showed that ~0.4% of the total ^{137}Cs was trapped in the crystallized $NaNO_3$ and was carried out in basic conditions.

Past studies (WHC-EP-0915) also demonstrated that $NaNO_3$ crystals can be cleanly decontaminated from all radionuclides, i.e., co-precipitation does not occur with $NaNO_3$. However, that study did not look specifically at the ^{90}Sr which appeared to co-precipitate to some extent with $NaNO_3$ crystals in the study reported here both in the initial precipitation with the evaporation apparatus and with recrystallization. The prior study looked at the total activity as the indicator for a clean salt and preformed multiple recrystallizations. Another difference in the studies is that the prior study was done under acidic conditions and this study was done under basic conditions, which may or may not make a difference in the ability to co-precipitate ^{90}Sr in $NaNO_3$ (this study does not address that question).

2. DESCRIPTION OF TESTS

The laboratory apparatus used in the 222-S hot cells is schematically shown in Figure 2-1. The diagrams of the experiments for each of the four solid phases are shown in Figures 2-2 through 2-5. The feed compositions are shown in Table 2-1. The parameters for the evaporation experiments, amount of spiking salt, condensate-to-feed ratio, and temperatures, were based on computer modeling using the OLI Environmental Simulation Program (ESP).[1]

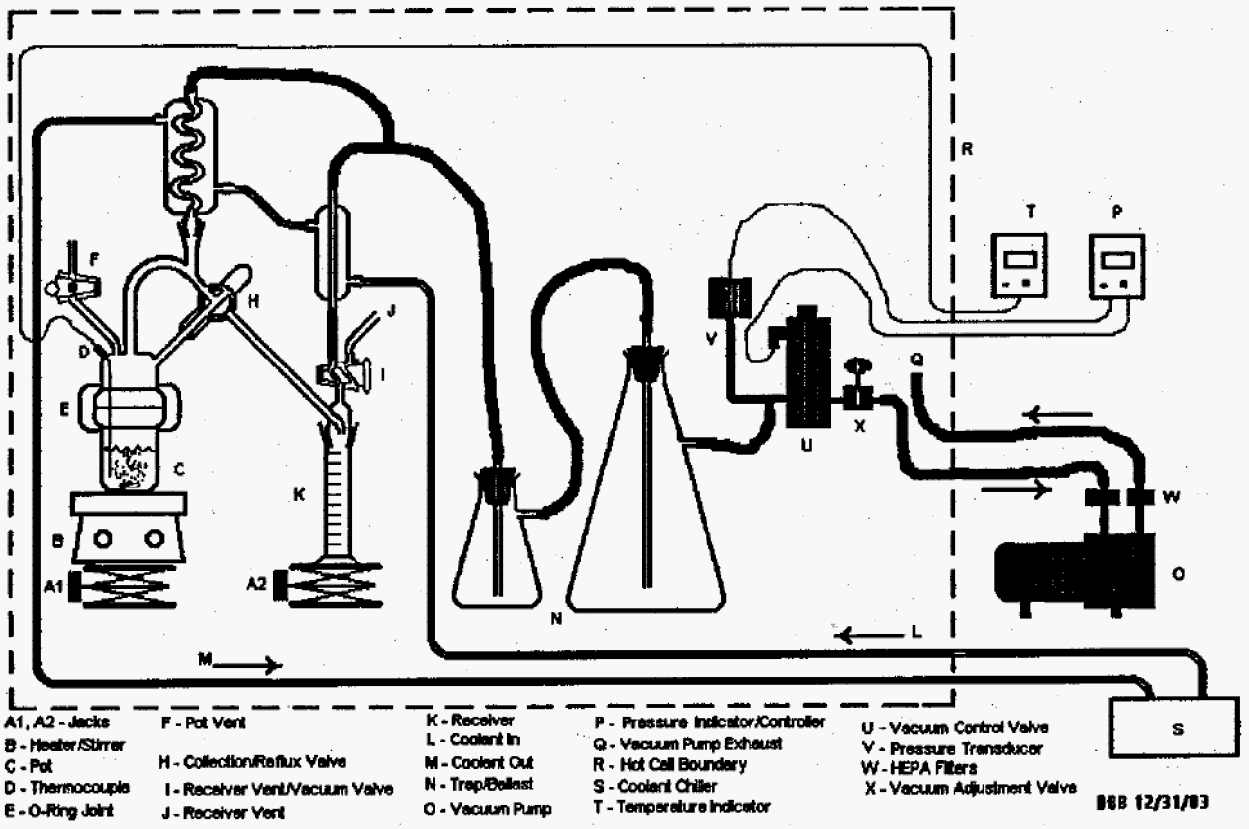

Figure 2-1. Schematic Drawing of Boildown Apparatus.

[1] Software product of OLI Systems, Inc., Morris Plains, New Jersey.

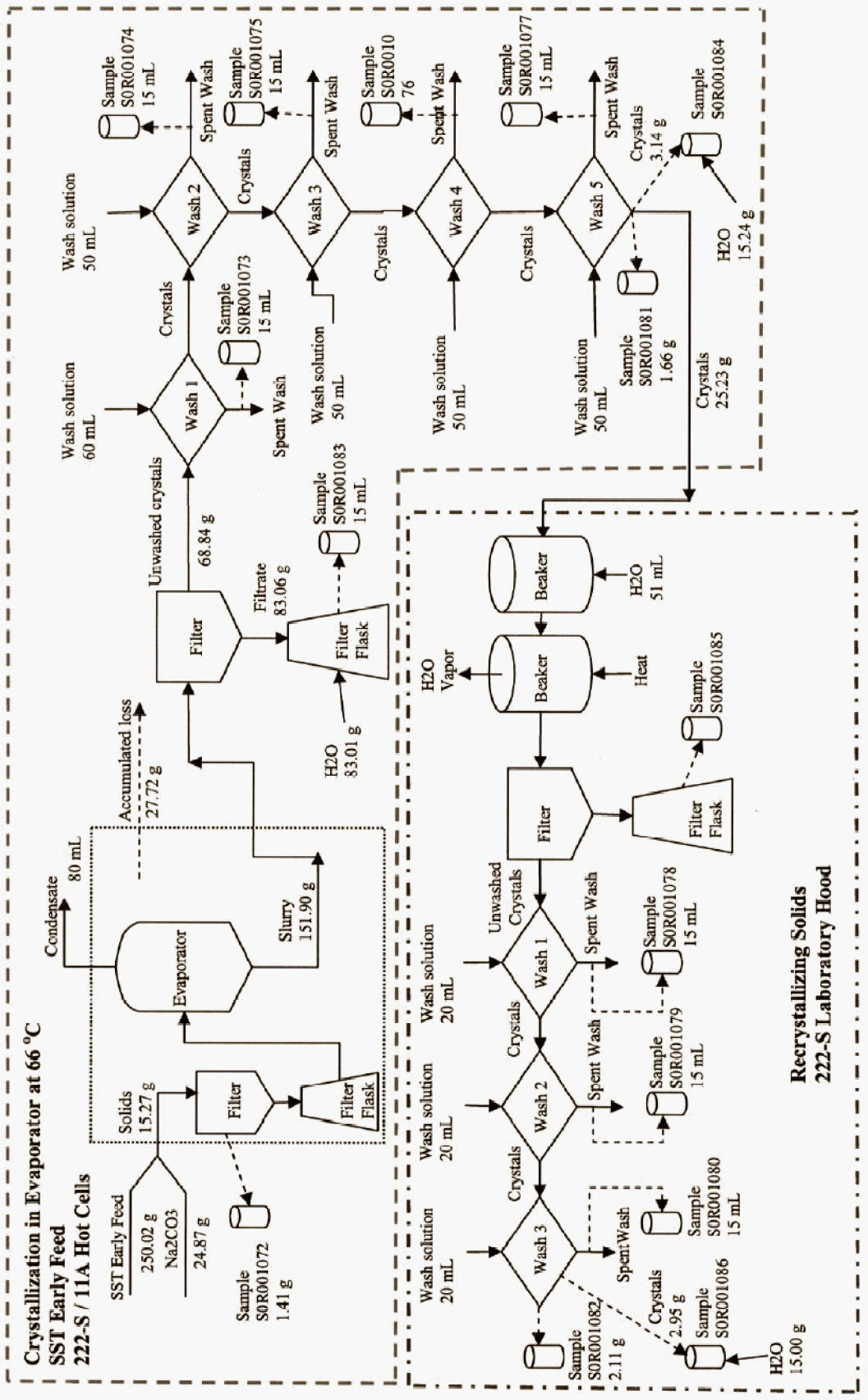

Figure 2-3. Diagram of the Na_2CO_3 Run.

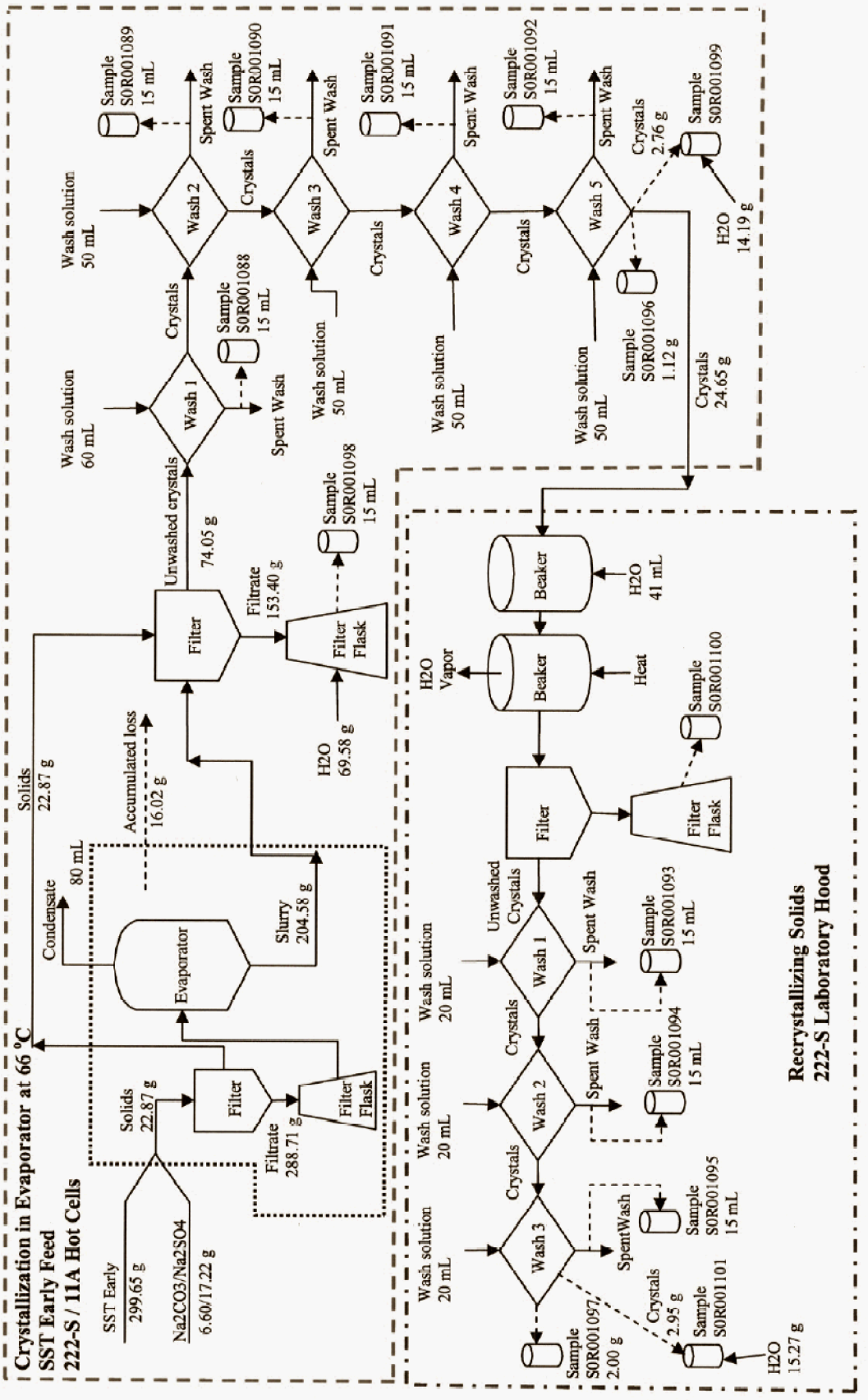

Figure 2-4. Diagram of the $Na_6CO_3(SO_4)_2$ Run.

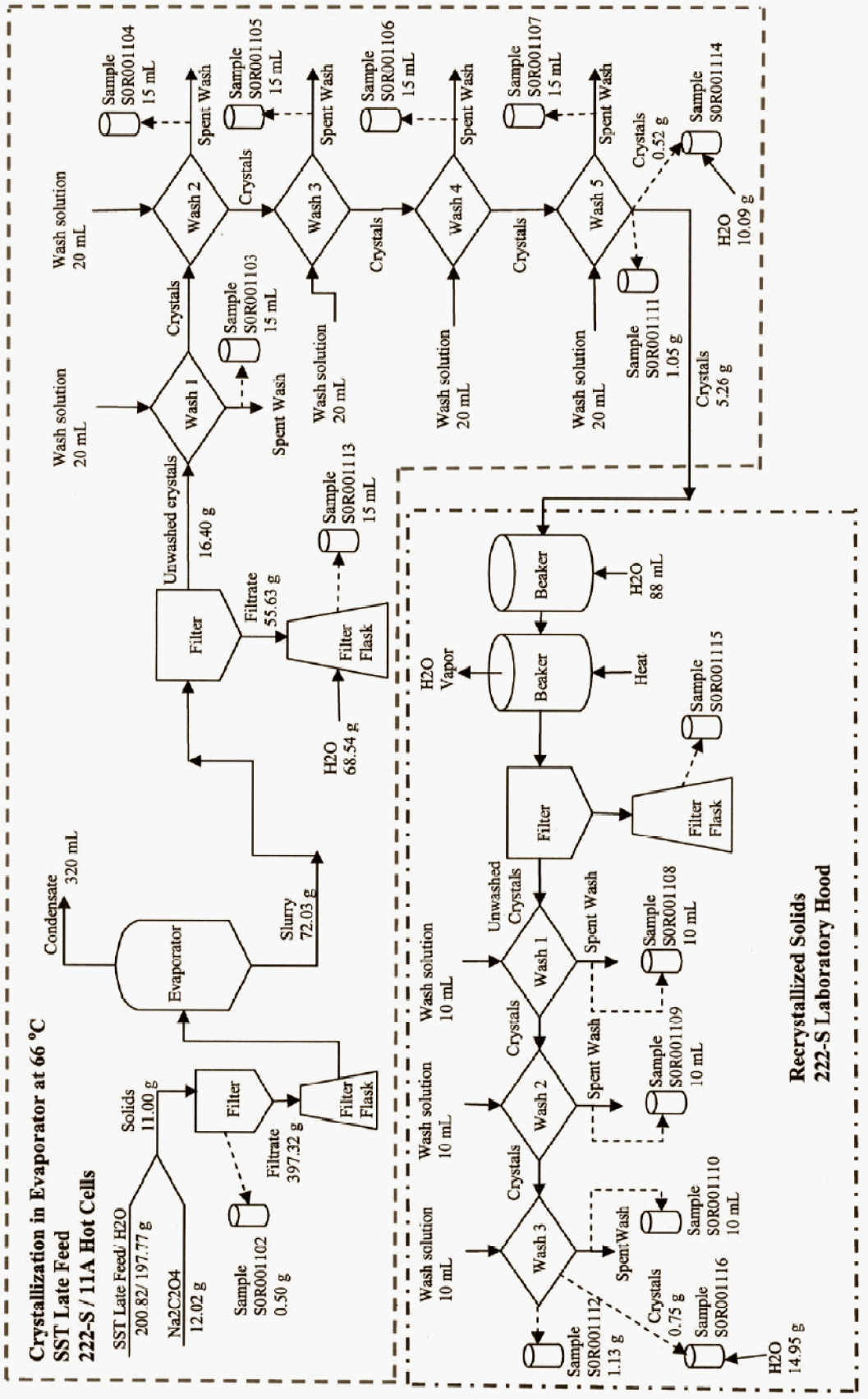

Figure 2-5. Diagram of the $Na_2C_2O_4$ Run.

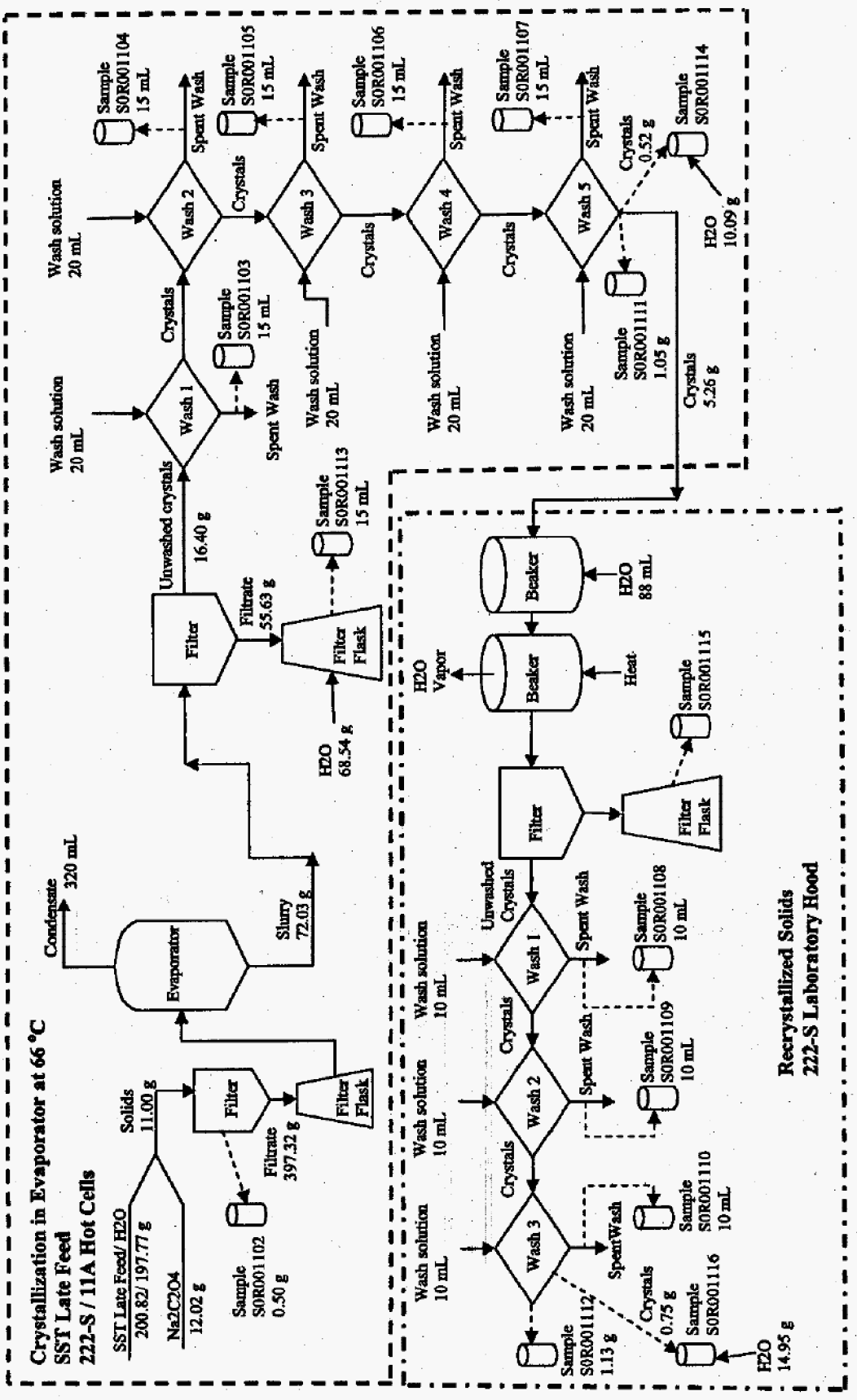

Figure 2-5. Diagram of the $Na_2C_2O_4$ Run.

Table 2-1. Composition of SST Early and SST Late Feed Solutions.
(Analyte concentrations in molarity, except as noted)

Analyte	SST Early	SST Late	Early/Late
Wt% H_2O	57.8	89.4	--
Density, g/mL	1.32	1.06	--
Al	0.289	0.039	7.4
Cr	0.019	0.003	6.3
K	0.018	0.003	6.0
Na	6.309	1.201	5.3
P	0.046	0.025	1.8
S	0.138	0.023	6.0
Si	0.006	0.002	3.0
F	0.010	0.052	0.2
Cl	0.073	0.013	5.6
NO_2	0.515	0.071	7.3
NO_3	3.276	0.530	6.2
PO_4	0.046	0.024	1.9
SO_4	0.128	0.021	6.1
Oxalate	0.006	0.054	0.1
CO_3	0.614	0.099	6.2
TOC	0.083	0.110	0.8
OH	0.618	0.100	6.2
^{137}Cs, µCi/mL	59.9	9.40	6.4
^{90}Sr, µCi/mL	0.060	0.008	7.5
^{129}I, µCi/mL	5.5E-5	6.9E-6	6.1
^{99}Tc, µg/mL	3.68	0.601	8.0
Mass balance	92.7	97.4	--
Charge balance (+/-)	0.98	0.97	--

Note: Table taken from RPP-RPT-31352, 2006, *Fractional Crystallization Flowsheet Tests with Actual Tank Waste.*

2.1 SODIUM NITRATE RUN

The sodium nitrate run began with a charge of 129.82 g (98.3 mL) of SST Early feed solution to the boiling pot and heated to 40 °C. While stirring, 32.26 g of $NaNO_3$ were slowly added until completely dissolved. The boiling pot was attached to the boildown apparatus in the reflux position and the pressure and heat was adjusted to maintain constant boiling at 40 °C. After steady boiling was achieved, the valve was switched to collect condensate position and monitored until ~39 mL were collected. The vacuum was released and the slurry was filtered with a jacketed filter apparatus at 40 °C. The filtrate was diluted with water to prevent precipitation and sampled. The filtered solids were washed five times with a saturated $NaNO_3$ solution. The washed crystals and each of the spent wash liquid were sampled for analysis and the washed crystals were loaded out of the 222-S 11A hot cells to a 222-S Laboratory ventilation

hood. X-ray diffraction (XRD) analysis on the washed crystals revealed them to be $NaNO_3$ with no other phases detected.

The washed crystals were then redissolved in water and stirred and heated to near boiling in an open beaker until a freely flowing wet slurry was formed. The slurry was then filtered and the filtrate was sampled. The filtered solids were washed three times with saturated $NaNO_3$ solution. The washed crystals and each of the spent wash liquids were sampled for analysis. The XRD analysis on the washed crystals revealed them to be $NaNO_3$ with no other phases detected.

2.2 SODIUM CARBONATE RUN

The sodium carbonate run began with a charge of 250.02 g (189 mL) of SST Early feed solution to the boiling pot and heated to 66 °C. While stirring, 24.87 g of anhydrous Na_2CO_3 were slowly added and continuously stirred for ~1 hr. The stirred boiling pot continued to be cloudy and was filtered with a jacketed filter apparatus at 66 °C. The filtered solids were sampled for XRD analysis and the filtrate was returned to the boiling pot. The XRD analysis on the crystals revealed them to be primarily $Na_2CO_3 \cdot H_2O$ with ~10% $NaNO_3$ detected (the nitrate phase was most likely the result of the filtered crystals not being washed). The boiling pot was attached to the boildown apparatus in the reflux position and the pressure and heat was adjusted to maintain constant boiling at 66 °C. After steady boiling was achieved, the valve was switched to collect condensate position and monitored until ~80 mL were collected. The vacuum was released and the slurry was filtered with a jacketed filter apparatus at 66 °C. The filtrate was diluted with water to prevent precipitation and sampled. The filtered solids were washed five times with a saturated Na_2CO_3 solution. The washed crystals and each of the spent wash liquids were sampled for analysis and the washed crystals were loaded out of the 222-S 11A hot cells to a 222-S Laboratory ventilation hood. The XRD analysis on the washed crystals revealed them to be ~80% $Na_2CO_3 \cdot H_2O$ with ~10% $Na_2CO_3 \cdot 10H_2O$ and ~10% $Na_6CO_3(SO_4)_2$; no other phases were detected.

The washed crystals were then redissolved in water and stirred and heated to near boiling in an open beaker until a freely flowing wet slurry was formed. The slurry was then filtered and the filtrate was sampled. The filtered solids were washed three times with saturated $NaNO_3$ solution. The washed crystals and each of the spent wash liquids were sampled for analysis. The XRD analysis on the washed crystals revealed them to be ~58% $Na_2CO_3 \cdot H_2O$ with ~40% $Na_2CO_3 \cdot 10H_2O$ and ~2% Na_2NO_3; no other phases were detected.

2.3 BURKEITE RUN

The $Na_6CO_3(SO_4)_2$ (burkeite) run began with a charge of 299.65 g (227 mL) of SST Early feed solution to the boiling pot and heated to 66 °C. While stirring, 6.60 g of anhydrous Na_2CO_3 and 17.22 g of anhydrous Na_2SO_4 were slowly added and continuously stirred for ~1 hr. The stirred boiling pot continued to be cloudy. The ESP program predicted that ~16 g of burkeite [$Na_6CO_3(SO_4)_2$] would precipitate out of solution at 66 °C. The contents of the boiling pot were filtered with a jacketed filter apparatus at 66 °C. The filtered solids were retained in the filter apparatus at 66 °C and the filtrate was returned to the boiling pot. The XRD sample of the filtered solids was inadvertently missed. The boiling pot was attached to the boildown apparatus

in the reflux position and the pressure and heat were adjusted to maintain constant boiling at 66 °C. After steady boiling was achieved, the valve was switched to collect condensate position and monitored until ~80 mL were collected. The vacuum was released and the slurry was added to the previously filtered solids and filtered at 66 °C. The filtrate was diluted with water to prevent precipitation and sampled. The filtered solids were washed five times with a saturated Na_2CO_3/Na_2SO_4 solution. The washed crystals and each of the spent wash liquid were sampled for analysis and the washed crystals were loaded out of the 222-S 11A hot cells to a 222-S Laboratory ventilation hood. The XRD analysis on the washed crystals revealed them to be $Na_6CO_3(SO_4)_2$ (burkeite) with no other phases detected.

The washed crystals were then redissolved in water and stirred and heated to near boiling in an open beaker until a freely flowing wet slurry was formed. The slurry was then filtered and the filtrate was sampled. The filtered solids were washed three times with saturated Na_2CO_3/Na_2SO_4 solution. The washed crystal and each of the spent wash liquid were sampled for analysis. The XRD analysis on the washed crystals revealed them to be $Na_6CO_3(SO_4)_2$ with no other phases detected.

2.4 SODIUM OXALATE RUN

The sodium oxalate run began with a charge of 200.82 g (189 mL) of SST Late feed solution and 200 mL of water to the boiling pot and heated to 66 °C. While stirring, 12.02 g of anhydrous $Na_2C_2O_4$ were slowly added and continuously stirred for ~1 hr. The stirred boiling pot continued to be cloudy and was filtered with a jacketed filter apparatus at 66 °C. The filtered solids were sampled for XRD analysis and the filtrate was returned to the boiling pot. The XRD analysis on the crystals revealed them to be primarily $Na_2C_2O_4$ with ~2% $NaNO_3$ detected (the nitrate phase was most likely the result of the filtered crystals not being washed). The boiling pot was attached to the boildown apparatus in the reflux position and the pressure and heat were adjusted to maintain constant boiling at 66 °C. After steady boiling was achieved, the valve was switched to collect condensate position and monitored until ~320 mL were collected. The vacuum was released and the slurry was filtered with a jacketed filter apparatus at 66 °C. The filtrate was diluted with water to prevent precipitation and sampled. The filtered solids were washed five times with a saturated $Na_2C_2O_4$ solution. The washed crystals and each of the spent wash liquids were sampled for analysis, and the washed crystals were loaded out of the 222-S 11A hot cells to a 222-S Laboratory ventilation hood. The XRD analysis on the washed crystals revealed them to be $Na_2C_2O_4$ with no other phases detected.

The washed crystals were then redissolved in water and stirred and heated to near boiling in an open beaker until a freely flowing wet slurry was formed. The slurry was then filtered and the filtrate was sampled. The filtered solids were washed three times with saturated $Na_2C_2O_4$ solution. The washed crystal and each of the spent wash liquid were sampled for analysis. The XRD analysis on the washed crystals revealed them to be $Na_2C_2O_4$ with no other phases detected.

3. TOTAL ACTIVITY AND RADIONUCLIDE ANALYSES

The filtrates and the dissolved washed crystals were analyzed as shown in Table 3-1 for tests 1-5. The spent wash solutions were analyzed for test 5, and the solids were analyzed for test 6.

Table 3-1. Analytical Methods for Washed Solids and Filtrate Samples.

Test	Procedure	Method	Analytes
1	La-548-121	Gamma energy analysis	γ-emitting radionuclides, including ^{137}Cs
2	LA-506-102	Inductively coupled plasma/mass spectroscopy	^{99}Tc
3	LA-378-103	Extraction/gamma counting	^{129}I
4	LA-220-101	Separation/beta counting	^{90}Sr
5	LA-548-111	Liquid scintillation	Total activity
6	LT-507-101	XRD	Solid phase identification

The sample analysis results are shown in Tables 3-2 and 3-3. The sample numbers can be referenced in the experimental diagrams shown in Figures 2-2 through 2-5.

The wash filtrates were analyzed for total activity, and the results are shown in Table 3-2 and plotted in Figures 3-1 and 3-2. Figure 3-1 appears to show that total activity drops rapidly for the first three washes and then levels off and approaches zero. Figure 3-2 displays the same general shape for the first three washes. It would appear that four to five washes are optimal.

Table 3-2. Results of Radionuclide Analyses for Filtrates and Solids.
(All units are µCi/mL except for Tc which is in µg/mL)

Run	Crystallization in Evaporator				Recrystallized Solids	
	Analyte	Feed[a]	Diluted Filtrate	Dissolved Washed Solids	Filtrate	Dissolved Washed Solids
$NaNO_3$	S06R00	SST Early	1,069	1,063	1,070	1,071
	^{137}Cs	59.9	40.3	0.0485	0.262	2.79E-04
	^{129}I	5.5E-05	3.97E-05	<1.99E-05	<8.63E-06	<2.08E-05
	^{99}Tc	3.67	2.61	3.02E-03	0.0180	<6.00E-04
	$^{89/90}Sr$	0.060	1.15E-03	4.10E-04	1.27E-03	6.23E-04
	Total activity	ND	49.7	0.0579	0.309	<9.93E-04
Na_2CO_3	S06R00	SST Early	1,083	1,084	1,085	1,086
	^{137}Cs	59.9	44.2	0.0320	0.0841	2.35E-04
	^{129}I	5.5E-05	4.74E-05	<2.27E-05	<1.67E-05	<1.92E-05
	^{99}Tc	3.67	2.92	2.09E-03	4.65E-03	<3.00E-04
	$^{89/90}Sr$	0.060	5.81E-04	6.93E-03	0.0117	1.16E-03
	Total activity	ND	54.0	0.0522	2.72E-03	2.72E-03
$Na_6CO_3(SO_4)_2$	S06R00	SST Early	1,098	1,099	1,100	1,101
	^{137}Cs	59.9	58.4	0.0190	0.359	7.98E-05
	^{129}I	5.5E-05	5.36E-05	<1.68E-05	<1.84E-05	<1.58E-05
	^{99}Tc	3.67	3.54	1.26E-03	0.0223	<3.00E-04
	$^{89/90}Sr$	0.060	5.33E-04	0.0151	3.65E-03	0.0296
	Total activity	ND	70.8	0.0521	0.449	0.0679
$Na_2C_2O_4$	S06R00	SST Late	1,113	1,114	1,115	1,116
	^{137}Cs	9.4	12.1	5.18E-03	0.0856	7.58E-05
	^{129}I	6.9E-06	1.09E-05	<1.91E-05	<2.47E-05	<1.93E-05
	^{99}Tc	0.601	0.794	<3.00E-04	4.30E-03	<3.00E-04
	$^{89/90}Sr$	0.008	1.72E-03	9.09E-04	1.33E-05	2.29E-03
	Total activity	ND	13.7	0.0129	0.0999	5.39E-03

[a] Taken from Table 2-1.

Table 3-3. Results of Total Activity Analyses for Wash Solutions.
(All units are µCi/mL)

Run	Crystallization in Evaporator					Recrystallized Solids		
	Wash Number					Wash Number		
	1	2	3	4	5	1	2	3
Sample Number	S06R00_	S06R00_	S06R00_	S06R00_	S06R00_	S06R00_	S06R00_	S06R00_
$NaNO_3$	1,058	1,059	1,060	1,061	1,062	1,064	1,065	1,066
	36.1	8.83	0.940	0.221	0.0995	0.0822	0.0133	2.17E-03
Na_2CO_3	1,073	1,074	1,075	1,076	1,077	1,078	1,079	1,080
	73.9	15.8	4.13	1.59	0.497	0.0877	0.0366	4.89E-03
$Na_6CO_3(SO_4)_2$	1,088	1,089	1,090	1,091	1,092	1,093	1,094	1,095
	62.2	17.7	5.21	1.37	0.501	0.0909	0.0235	6.86E-03
$Na_2C_2O_4$	1,103	1,104	1,105	1,106	1,107	1,108	1,109	1,110
	8.17	1.38	0.769	0.467	0.345	7.13E-03	1.71E-03	7.71E-04

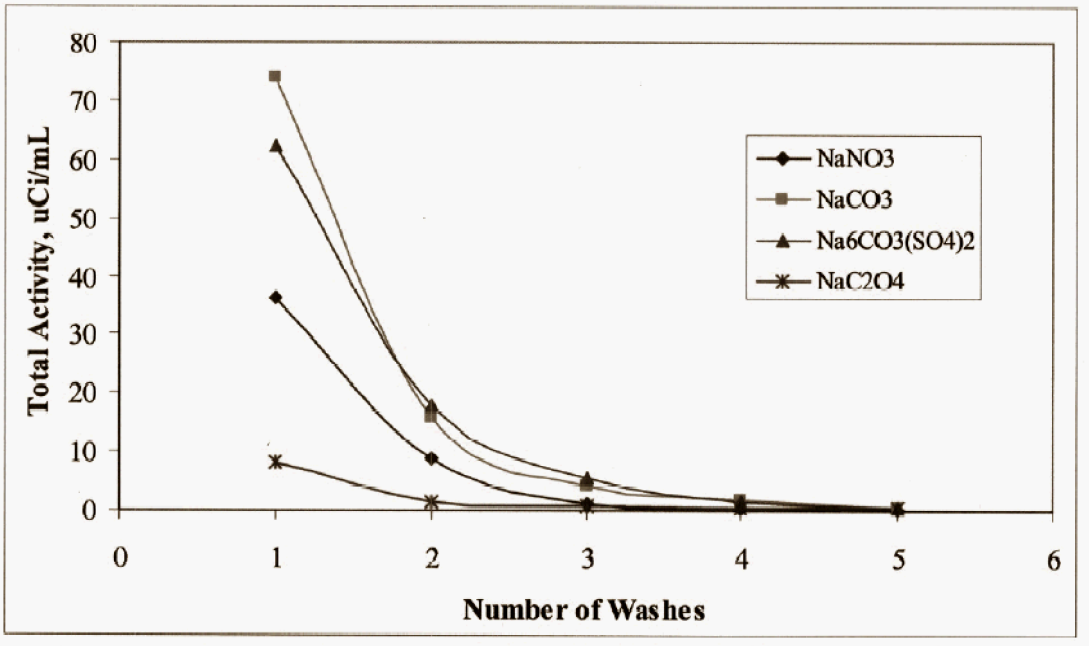

Figure 3-1. Total Activity vs. Number of Washes for Evaporation Samples.

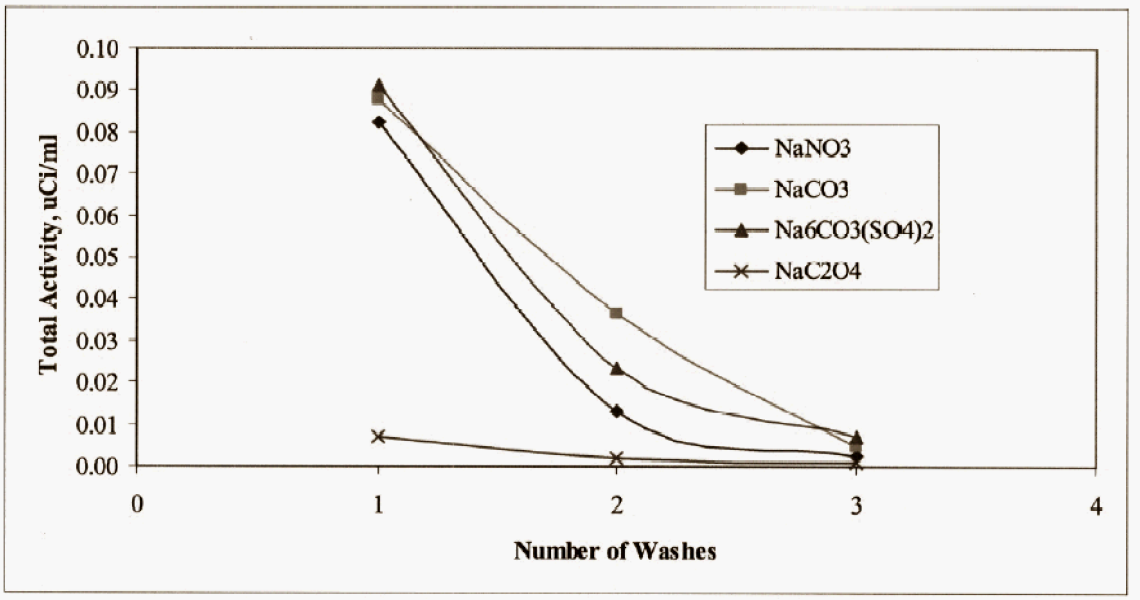

Figure 3-2. Total Activity vs. Number of Washes for Wash Samples.

4. RESULTS

One way to measure the extent to which the radionuclides are being included in the crystalline solids is to calculate a decontamination factor (DF) for the radionuclides. The DF can be defined as the μCi/mL of a given radionuclide in the original liquid tank waste (the fractional crystallization feed stream) divided by the μCi/mL of that radionuclide in the supplemental treatment stream (the product of fractional crystallization) when both streams are adjusted to a common sodium concentration. Thus, for ^{137}Cs:

$$DF_{Cs} = [^{137}Cs, \mu Ci/mL/Na, molar]_{feed} / [^{137}Cs, \mu Ci/mL/Na, molar]_{product}$$

For these experimental runs the DF can be defined as the μCi/mL of a given radionuclide in the feed solution (SST Early or SST Late) divided by the μCi/mL of that radionuclide in the product of fractional crystallization (the washed solids) when both streams are adjusted to a common sodium concentration. The larger the value of DF for a radionuclide, the less that radionuclide is ending up in the crystallized product either by inclusion or by co-precipitation. The DFs for ^{137}Cs and ^{90}Sr are summarized in Table 4-1.

Table 4-1. Estimated Decontamination Factors and Percent of Initial Radionuclides Trapped in the Solids.

Run	Feed	DF_{Cs}	%Cs in Solids	DF_{Sr}	%Sr in Solids
$NaNO_3$	SST Early	190	0.4	23.	3
Na_2CO_3	SST Early	510	0.2	2.4	37
$Na_6CO_3(SO_4)_2$	SST Early	760	0.07	0.96	56
$Na_2C_2O_4$	SST Late	440	0.2	2.2	42

Notes:
Assumptions:
(1) Addition of spiking salts does not change the volume of the feed solution.
(2) Filtered solids are 80% by wt for filtered solids for $NaNO_3$ and Na_2CO_3 and 70% by wt for filtered solids for $Na_6CO_3(SO_4)_2$ and C_2O_4 for purposes of calculating the moles of Na in the solids.
(3) Addition of solids to liquid samples adds to the volume by wt solids/2.
(4) Losses in total filtered unwashed solids are due to wet solids remaining in the evaporation apparatus glassware.

For the SST Early composite, the DF_{Cs} is related to the weight percent of solids in the slurry. The greater the weight percent of solids in the slurry, the smaller the DF_{Cs} or the amount of phase separation. This is because of the amount ^{137}Cs carried in the interstitial liquid with the filtered solids. An example of the DF calculation for ^{137}Cs in the $NaNO_3$ run is shown in the following. The input data and sample numbers can be found in Table 3-2 and Figure 2-2, and the assumptions made for the purposes of these calculations are summarized in the notes for Table 4-1.

$NaNO_3$ run SST Early Feed:

The Na concentration is calculated from the analysis of the SST Early sample plus the number of moles of Na added as $NaNO_3$. The final volume of the feed solution is approximated by multiplying the weight of the spiking salt by 0.5 mL/g (e.g., for 32.26 g of $NaNO_3$, the volume is adjusted by adding 26.13 mL).

$$Na(moles/L) = \frac{[(6.309\,moles/L)\,x\,(98.3\,mL)\,x\,(1\,L/1000\,mL) + (32.26\,g\,NaNO_3)/(85.01\,g/mole)]}{[(98.3\,mL + (32.26\,g\,NaNO_3\,x\,0.5\,mL/g))\,x\,(1\,L/1000\,mL)]} = 8.74\,moles/L$$

The µCi/mL of ^{137}Cs in the feed is calculated from the analysis the SST Early sample multiplied by the SST Early feed added divided by the adjusted volume of the feed.

$$Cs\,(\mu Ci/mL) = (59.9\,\mu Ci/mL)\,x\,\frac{(98.3\,mL\,SST\,Early\,vol.)}{98.3\,mL + (32.26\,g\,NaNO_3\,x\,0.5\,mL/g)} = 51.5\,\mu Ci/mL$$

$NaNO_3$ run SST Early Product:

The washed $NaNO_3$ crystals were sampled (S06R001063) by adding 2.75 g of the wet crystals to 14.79 mL of H_2O and dissolving. The number of moles of Na in the sample were estimated by approximating the dry weight of the washed crystals by assuming the dry weight is 80% of the wet weight. The sample volume is adjusted, as shown above, by multiplying the weight of the crystals by 0.5 mL/g.

$$Na\,(moles/L) = \frac{[(2.75\,g\,wet\,washed\,NaNO_3)\,x\,(0.8\,g\,dry/1\,g\,wet\,NaNO_3)]/(85.01\,g/mole,NaNO_3)}{[(14.75\,mL\,H_2O + (2.75\,g\,dry\,NaNO_3\,x\,0.5\,mL/g))\,x\,(1\,L/1000\,mL)]} = 1.60\,moles/L$$

The µCi/mL of ^{137}Cs in the product is just the results of the analysis of sample S06R001063.

$$Cs\,(\mu Ci/mL) = 0.0485\,\mu Ci/mL$$

The DF_{Cs} is then calculated as

$$SF_{Cs} = \frac{[(51.46\,\mu Ci/mL, Cs)/(8.74\,moles/L, Na)]_{FEED}}{[(0.0485\,\mu Ci/mL, Cs)/(1.63\,moles/L)]_{PRODUCT}} = 194\,or \cong 190$$

Another way to measure the extent that a radionuclide is being co-precipitated or included with one of the solid phases is to calculate the percentage of radionuclide that ends up in the crystallized product. The approximated percentages of the radionuclides ^{137}Cs and ^{90}Sr are also shown in Table 4-1 for each of the experimental runs. An example of the calculation of ^{90}Sr percentage in the $Na_2C_2O_4$ run is show in the following. The input data and sample numbers can be found in Table 3-2 and Figure 2-5.

$Na_2C_2O_4$ run SST Late Feed:

The µCi of ^{90}Sr in the feed is calculated from the analysis of the SST Late feed and the volume of the SST Late feed added.

$$Sr\,(\mu Ci\ in\ feed) = (0.008\ \mu Ci / mL\ in\ feed)\ x\ [(200.82\ g\ feed) / 1.06\ g / mL\ feed\ density] = 1.52\ \mu Ci$$

$Na_2C_2O_4$ run SST Late Product:

The washed $Na_2C_2O_4$ crystals were sampled (S06R001114) by adding 0.52 g of the wet crystals to 10.09 mL of H_2O and dissolving. The volume of sample was approximated by adjusting the volume of the water plus the weight of the dry crystals added multiplied by 0.5 mL/g solids.

$$Adj.smpl.vol. = 10.09\ mL\ H_2O + [(0.52\ g\ Na_2C_2O_4)\ x\ (0.5\ mL / g\ solids)] = 10.35\ mL$$

The µCi of ^{90}Sr in the product $Na_2C_2O_4$ crystals is then calculated from the analysis of the S06R001114 sample and multiplied by the ratio of the total weight of filtered wet $Na_2C_2O_4$ crystals to that of the wet $Na_2C_2O_4$ crystals added to the sample. The total weight of the wet $Na_2C_2O_4$ crystals was approximated by adding the weight of the recovered filtered crystal plus accumulated losses due to unrecovered material from the glassware. It is assumed that the bulk of the unrecovered material is in the form of wet $Na_2C_2O_4$ crystals for the purposes of these calculations.

$$Sr\,(\mu Ci\ in\ product) = (0.000909\ \mu Ci / mL)\ x\ (10.35\ mL)\ x \left[\frac{(27.40\ g\ wet\ Na_2C_2O_4\ solids\ weighed + 7.58\ g\ solids\ lost)}{(0.52\ g\ wet\ solids\ sampled)}\right]$$

$$Sr\,(\mu Ci\ in\ product) = 0.633\ \mu Ci$$

So the % ^{90}Sr in the product $Na_2C_2O_4$ crystals is

$$\%Sr\ (in\ product) = 100 \times \left[\frac{0.633\ \mu Ci}{1.52\ \mu Ci}\right] = 42\%$$

Still another way to measure the extent that a radionuclide is being co-precipitated or included with one of the solid phases is to compare the ratios of the radionuclide concentrations to one another. It is obvious that ^{137}Cs, with a DF ≥190 for all four solid phases and <1% trapped in the solids, is not being significantly incorporated into the solids. So if the ratios of the other radionuclides that are present at significant levels (^{129}I, ^{99}Tc, and ^{90}Sr) in the SST Early and Late feeds are calculated, any incorporation of a radionuclide in either the filtrates or filtered solids will show up as decreasing in the filtrate and increasing in the washed solids. Table 4-2 shows the calculated ratios of the radionuclides to ^{137}Cs using the analysis results from Table 3-2.

Table 4-2. Ratios of Radionuclides to Cesium-137.

Run	Crystallization in Evaporator				Recrystallized Solids	
	Radionuclide	Feed	Filtrate	Washed Solids	Filtrate	Washed Solids
$NaNO_3$	S06R00____	SST Early	1,069	1,063	1,070	1,071
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	9.18E-07	9.85E-07	----	----	----
	^{99}Tc	6.13E-02	6.48E-02	6.23E-02	6.87E-02	----
	$^{89/90}Sr$	1.00E-03	2.85E-05	8.45E-03	4.85E-03	2.2
Na_2CO_3	S06R00____	SST Early	1,083	1,084	1,085	1,086
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	9.18E-07	1.07E-06	----	----	----
	^{99}Tc	6.13E-02	6.61E-02	6.53E-02	5.53E-02	----
	$^{89/90}Sr$	1.00E-03	1.31E-05	2.17E-01	1.39E-01	4.9
$Na_6CO_3(SO_4)_2$	S06R00____	SST Early	1,098	1,099	1,100	1,101
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	9.18E-07	9.18E-07	----	----	----
	^{99}Tc	6.13E-02	6.06E-02	6.63E-02	6.21E-02	----
	$^{89/90}Sr$	1.00E-03	9.13E-06	7.95E-01	1.02E-02	371.
$Na_2C_2O_4$	S06R00____	SST Late	1,113	1,114	1,115	1,116
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	7.34E-07	9.01E-07	----	----	----
	^{99}Tc	6.39E-02	6.56E-02	----	5.02E-02	----
	$^{89/90}Sr$	8.51E-04	1.42E-04	1.75E-01	1.55E-04	30.

The ratios for ^{129}I and ^{99}Tc remain essentially the same in the liquid and solid phases, whereas the ratios for ^{90}Sr decrease in the liquid phases and increase in the solids phases indicating that it is co-precipitating with each of the four solid phases.

An easier way to visualize the ratios is to calculate the ratios scaled to the feed solution so that all the ratios equal 1.00 for the feed solutions and for the ^{137}Cs. As an example, taking the ratio in Table 4-2 for the $NaNO_3$ run for ^{129}I in the filtrate and dividing it by the ratio in the SST Early feed solution gives $9.85 \times 10^{-07} / 9.18 \times 10^{-07} = 1.07$ which indicates that ratio $^{129}I/^{137}Cs$ is nearly the same in the SST Early feed solution as it is in the filtrate. As another example, for the $Na_6CO_3(SO_4)_2$ run for washed solids and ^{90}Sr: $7.95 \times 10^{-01} / 1.00 \times 10^{-03} = 793$ which indicates that the concentration of ^{90}Sr compared to ^{137}Cs in the washed crystals is 793 times greater than it was in the feed solution. Table 4-3 shows the results for all the values.

Table 4-3. Ratios of Radionuclides to Cesium-137 Normalized to Feed Solution.

Run	Crystallization in Evaporator				Recrystallized Solids	
	Radionuclide	Feed	Filtrate	Washed Solids	Filtrate	Washed Solids
$NaNO_3$	S06R00	SST Early	1,069	1,063	1,070	1,071
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	1.00	1.07	--	---	--
	^{99}Tc	1.00	1.06	1.02	1.12	--
	$^{89/90}Sr$	1.00	0.03	8.4	4.84	2,230.
Na_2CO_3	S06R00				1,085	1,086
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	1.00	1.17	--	--	--
	^{99}Tc	1.00	1.08	1.07	0.90	----
	$^{89/90}Sr$	1.00	0.01	216.	138.89	4,930.
$Na_6CO_3(SO_4)_2$	S06R00				1,100	1,101
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	1.00	1.00	--	--	--
	^{99}Tc	1.00	0.99	1.08	1.01	--
	$^{89/90}Sr$	1.00	0.01	793.	10.15	370310.
$Na_2C_2O_4$	S06R00				1,115	1,116
	^{137}Cs	1.00	1.00	1.00	1.00	1.00
	^{129}I	1.00	1.23	--	--	--
	^{99}Tc	1.00	1.03	--	0.79	--
	$^{89/90}Sr$	1.00	0.17	206.	0.18	35,500.

5. CONCLUSIONS

The test results conclusively show, with actual tank waste samples, that the four common sodium phases $NaNO_3$, Na_2CO_3, $Na_6CO_3(SO_4)_2$, and $Na_2C_2O_4$ do show a small amount of inclusion of radionuclides. This is shown by DF_{Cs} of between 190 and 760 and with <1% inclusion of the ^{137}Cs in the feed into the washed solids. While there definitely are inclusions, such is the nature of crystals, the separations criteria (for ^{137}Cs and sodium) of $<1.23 \times 10^{-3}$ Ci/mol Na were exceeded in all four of the tests performed as shown in Table 5-1. The results shown in Table 4-3 indicate that the ^{129}I and ^{99}Tc radionuclides closely follow the ^{137}Cs since their ratios are nearly equal to 1 in the feed and filtrate as well in the recrystallized solids and filtrate.

Table 5-1. All Tests Exceed Cesium-137 Activity in Product Performance Criteria.

Run	Feed	^{137}Cs Activity in Product (Ci/mole Na)	^{137}Cs Activity in Product Criteria (Ci/mole Na)
$NaNO_3$	SST Early	3.0E-05	<1.23E-3
Na_2CO_3	SST Early	1.3E-05	<1.23E-3
$Na_6CO_3(SO_4)_2$	SST Early	1.0E-05	<1.23E-3
$Na_2C_2O_4$	SST Late	9.9E-06	<1.23E-3

The tests conclusively show that ^{90}Sr does co-precipitate with all four solid phases. This is shown by the disappearance of 83–99% of the ^{90}Sr from the filtrate when compared to ^{137}Cs and an increase of 8–790 times that of ^{137}Cs in the solid phases. On recrystallization, the increase is 2,230–370,310 times that of the ^{137}Cs radionuclide in the solid phases. Although ^{90}Sr co-precipitates with the $NaNO_3$ solid phase, it is not as extensive as the other phases, probably because Sr^{+2}/Na^+ ion substitution in the $NaNO_3$ crystal lattice is the only driving force. The Sr^{+2} ionic radius (1.16 angstroms) is much closer to the Na+ ionic radius (0.99 angstroms) than for Cs+ (1.7 angstroms) or for Tc^{+4} or Tc^{+7} (0.64 and 0.56 angstroms). The ionic radii are from Acta Crystallographica, *Effective Ionic Radii in Oxides and Fluoride.* The other solid phases, $SrCO_3$ (0.00109 g in 100 mL H_2O at 24 °C), $SrSO_4$ (0.0138 g in 100 mL H_2O at 30 °C), and SrC_2O_4 (0.00575 g in 100 mL H_2O at 32 °C), are low solubility salts compared to $Sr(NO_3)_2$ (88.6 g in 100 mL H_2O at 30 °C), which add an additional driving force. The solubilities are from the American Chemical Society, *Solubilities of Inorganic and Metal-Organic Compounds.* There are no corresponding low-solubility Cs^+ salts.

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